The effect of element substitution on Ti-in-zircon geothermometry in volcanic zircons from Mount Pinatubo, Philippines

S.L. Lee and K. Hattori*

University of Ottawa, Ottawa, Canada *(*corresponding email: llee088@uottawa.ca)*

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uOttawa

Introduction

Background

- Ti-in-zircon geothermometry is widely used for estimating crystallization temperature (T_{xtal}) of zircon.
- Ferry and Watson (2007) suggest Ti^{4+} in the Si^{4+} site in zircon by the following substitution:

$$TiO_2 + ZrSiO_4 = ZrTiO_4 + SiO_2$$

$$(\text{Rutile} + \text{Zircon} = Ti^{IV}\text{-zircon} + \text{Quartz})$$

- Given accurate estimates of TiO_2 activity (a_{TiO_2}), SiO_2 activity (a_{SiO_2}) and pressure (P), the geothermometer has a precision of ± 5°C.

Research Problem

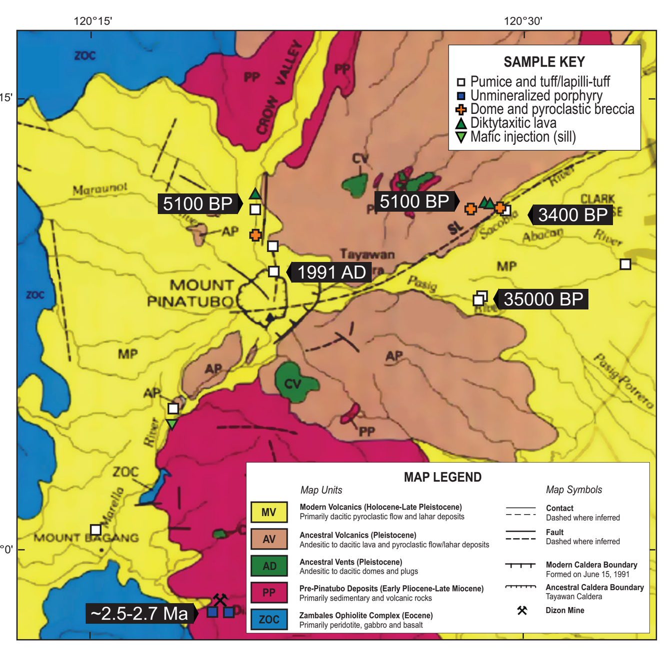
- Fu et al. (2008) documented very low T_{xtal} of zircons from intermediate to felsic igneous rocks (653 ± 124°C).
- Underestimation of the Ti-in-zircon geothermometer is a problem for "out-of-context" (detrital) zircons, especially in ancient rocks that do not have constraints on magmatic conditions.

Objectives

- To evaluate the effect of trace elements (REE+Y, U, Th, Hf) on the Ti-in-zircon geothermometer
- To evaluate a_{TiO_2} in Mount Pinatubo magma
- To assess the applicability of Ti-in-zircon geothermometry in ancient rocks

Geology and Sampling

- Mount Pinatubo is a stratovolcano (active since ~ 4 Ma) that is primarily composed of dacitic volcanic rocks.
- The early Pliocene (> 2.7-2.5 Ma) paleo-Pinatubo volcanics are found at Dizon Porphyry Cu Mine, located ~20 km south of the 1991AD crater.



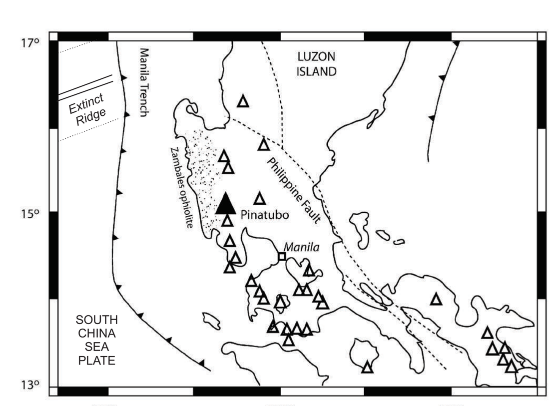


Figure 1: **[left]** Geology of Mount Pinatubo and surrounding area (modified from Newhall et al., 1996) **[right]** Regional setting of Mount Pinatubo (modified from De Hoog et al., 2004). Arc volcanism is related to eastward subduction of the South China Sea oceanic lithosphere along the Manila Trench in the Taiwan-Luzon Arc.

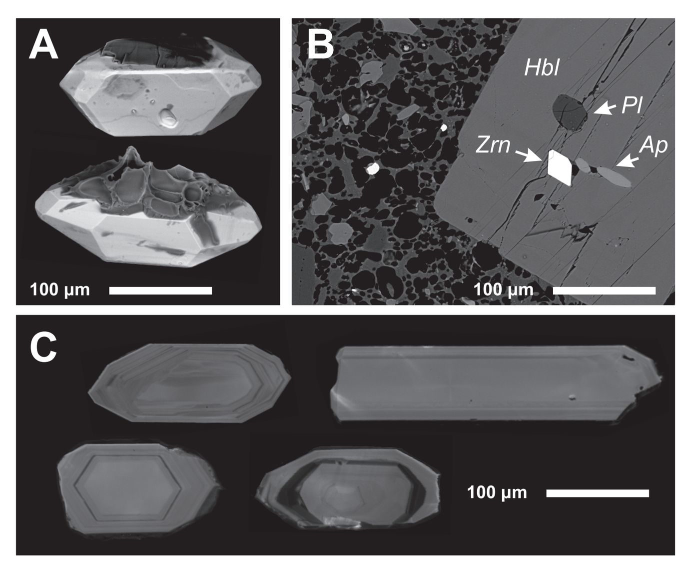
- We collected dacitic pumice (1991AD to 35000YBP) and least-altered Qz-diorite porphyry (> 2.7-2.5 Ma).
- Younger samples were collected from pyroclastic flow and fluvial deposits along major drainages from the modern volcano, while the oldest samples were collected from outcrops and talus debris at Dizon Porphyry Cu Mine.

Analytical Methods

- **Zircon** grains (n = 111) are examined with SEM-CL to select those without sector zoning. Trace element concentrations are determined using LA-ICP-MS (Excimer laser & Agilent 7700x ICP-MS) with 32 μm beam size and 10 Hz repetition rate. Elemental concentrations are obtained using NIST 612 glass reference and zircon Si content. GSD1G glass and 91500 zircon data indicate that the accuracy and precision of our data including Ti is ± 10%.
- **Fe-Ti-oxides** (unexsolved pairs that are in contact, n = 43) are analyzed for major and minor elements using EPMA (JEOL 8230).
- **Matrix glass** (n = 116) are analyzed for major elements using SEM-EDX (JEOL 6610LV) and trace elements using LA-ICP-MS with 50 s lines, 50 μm beam size, 15 Hz repetition rate, normalized to ^{42}Ca and standardized to NIST 612 glass. Ti values obtained for NIST 610, GSD1G and BCR2G suggest ± 3% precision and ± 7% accuracy.

Ti-in-Zircon Geothermometry

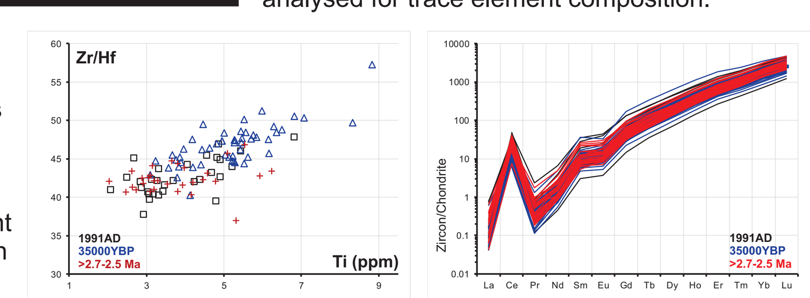
- Mount Pinatubo eruption products yield Ti-in-zircon T_{xtal} of 663-690°C (oldest to youngest) using the geothermometer of Ferry & Watson (2007), (a_{TiO_2} = 0.6, a_{SiO_2} = 1.0 and -40°C (-5°C/kbar) correction for low P ~ 2kbar).



- Magmatic T estimates based on cummingtonite suggest T of ~ 780°C.
- T_{xtal} underestimated by > 100°C.
- This suggests low Ti content in zircon *(crystallographic control)* or an overestimated a_{TiO_2} value *(melt composition control).*

Figure 2: SEM images of zircon grains used in this study **[A]** Low-vacuum images reveal grains in equilibrium with hornblende and matrix glass. **[B]** Zircon inclusion in hornblende **[C]** Only grains showing growth zoning and no sector zoning were analysed for trace element composition.

Figure 3: **[left]** Ti concentrations (2.0-8.8 ppm) and Zr/Hf weight ratios are positively correlated (r^2 = 0.551). This is interpreted as cooling of magma associated with differentiation/fractional crystallization. **[right]** Zircon REE plots (chondrite-normalized) show enrichment in HREE, typical of igneous zircon. High Ce/Ce* suggests oxidized magmas.



- Degree of T underestimation (ΔT) is inversely correlated with REE+Y and U+Th, suggesting these elements are not contributing to Ti-in-zircon geothermometry.
- Positive correlation between ΔT and Hf suggests increasing incompatible elements in the melt during its cooling.

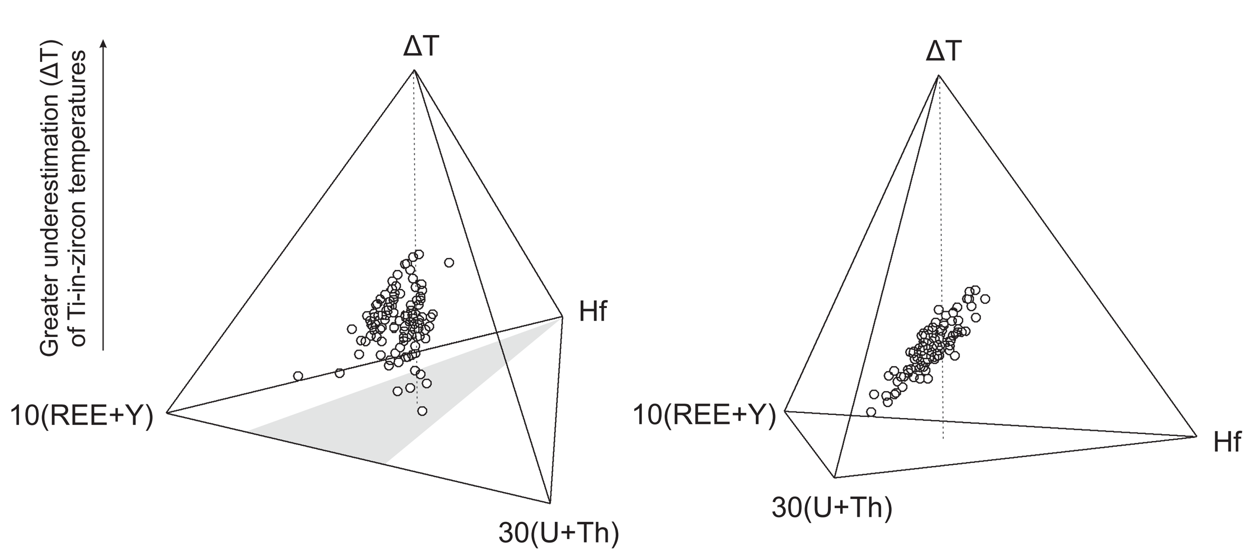
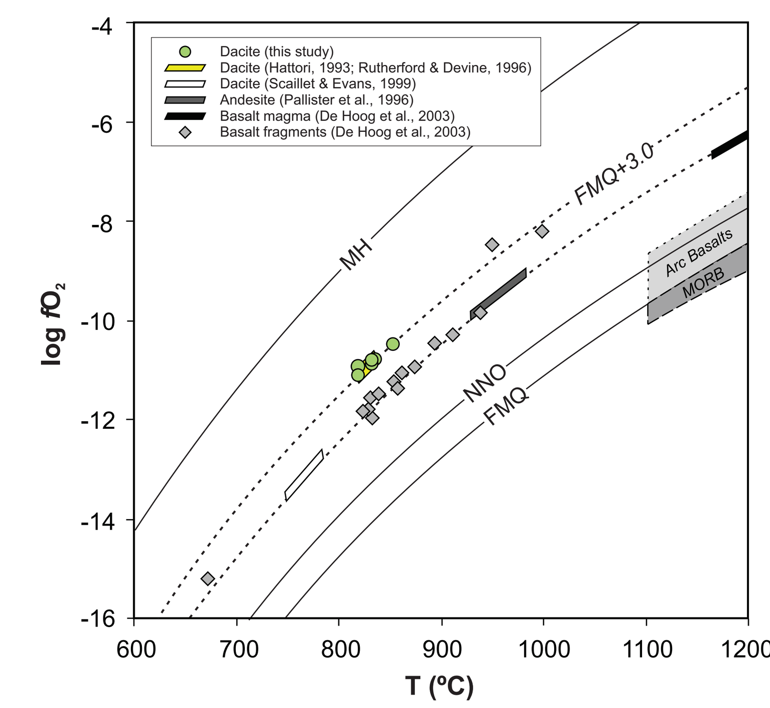


Figure 4: Quaternary diagram of ΔT, 10(REE+Y), 30(U+Th) and Hf. Dotted vertical axis indicates increasing ΔT, and grey space is the projection of data onto the basal ternary diagram.

- This suggests a non-crystallographic control on the underestimation of T.
- a_{TiO_2} as low as ~ 0.2 is required to yield T_{xtal} ranging ~ 750-800°C.

Fe-Ti-Oxide Thermobarometry

- Co-existing pairs of unexsolved Fe-Ti-oxides yield magmatic T ranging ~ 790-825°C (± 60°C), with no systematic relationship to eruptive age.
- Calculated Fe-Ti-oxide compositions are low in Ti, with X_{ulv} = 0.07-0.13 and X_{ilm} = 0.49-0.53.



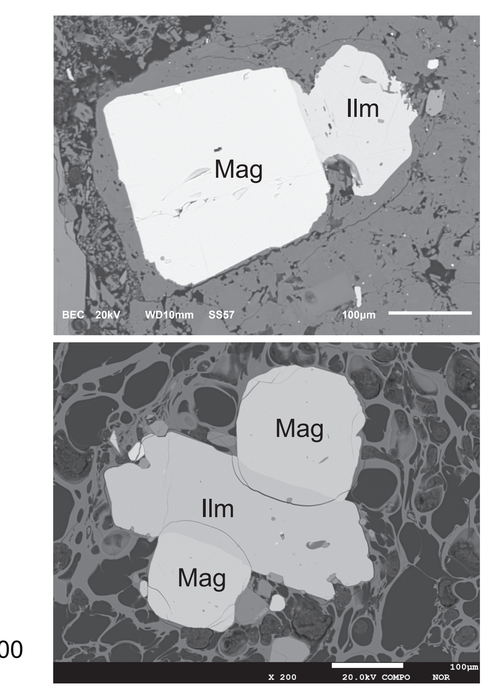


Figure 5: **[left]** Calculated T from co-existing Fe-Ti-oxide pairs (green circles) compared to 1991AD values from other studies (see symbol key) and common mid-ocean ridge (e.g. Bezos and Humler, 2005) and arc basalt fields; modified from De Hoog et al. (2003) **[right]** BSE images of Fe-Ti-oxide pairs in equilibrium, from 35000YBP (top) and 5100YBP (bottom) eruption products

- Using the method of Wark et al. (2007) and thermodynamic data from Holland and Powell (1998), Fe-Ti-oxides of all eruption products are used to calculate melt a_{TiO_2} ranging 0.23-0.32.
- These values are significantly lower than the suggested minimum a_{TiO_2} of 0.5-0.6 for most silicic igneous crustal rocks.
- Using a_{TiO_2} = 0.23-0.32, the Ti-in-zircon geothermometer yields T_{xtal} ranging 719-751°C (0.32) and 752-786°C (0.23), which are consistent with T acquired using cummingtonite and Fe-Ti-oxides.

Titanium in Matrix Glass

- Ti concentrations are measured in homogeneous matrix glasses from young eruption products (1991AD, 5100YBP and 35000YBP).
- Ti ranges ~ 700-1000 ppm (Q_1-Q_3) and shows no systematic variation with increasing distance from Fe-Ti-oxides.

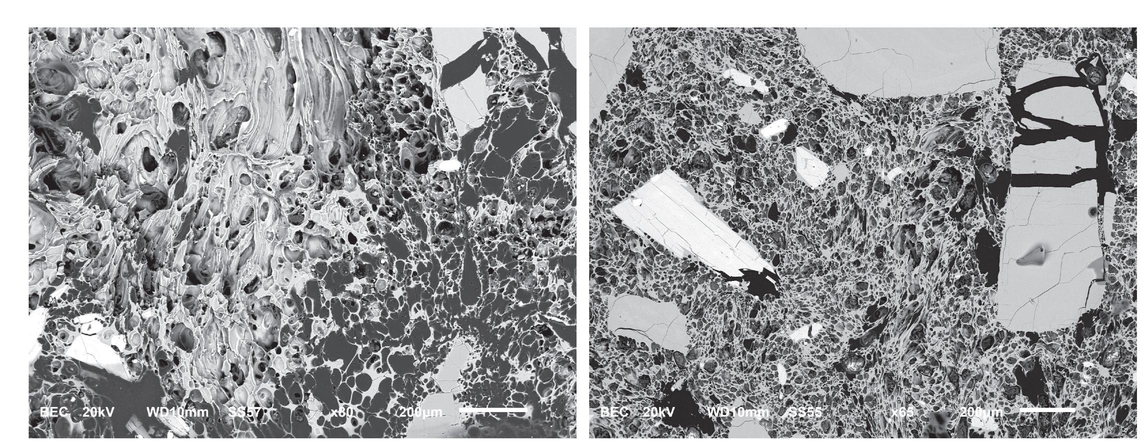


Figure 6: BSE images of matrix glasses in dacitic pumices from 1991AD (left) and 5100YBP (right)

- Using the method of Hayden et al. (2007) and an assumed T = 780°C, TiO_2 solubility at ~ 1360-1770 ppm Ti in melt is calculated.
- Using Ti concentrations in matrix glass and calculated TiO_2 solubility, a_{TiO_2} estimates range 0.60-0.68.
- The discrepancy between estimates from Fe-Ti-oxides and matrix glass may be explained by a difference in pressure between Mount Pinatubo reservoirs (~ 2 kbar) and calibration (10 kbar). Experiments by Green and Adam (2002) show that TiO_2 solubility increases at lower pressures (up to ~ 0.5 wt.% TiO_2 per 10 kbar), which would lower calculated a_{TiO_2}.

Zircon Saturation Temperature

- Zircon saturation T is calculated based on matrix glass compositions and bulk rock compositions using the method of Watson and Harrison (1983).
- The former yields saturation T of 756-759°C (54-94 ppm Zr, Q_1-Q_3), which is comparable to the latter, which ranges 738-760°C.
- These zircon saturation T are much higher than Ti-in-zircon T_{xtal} calculated using a_{TiO_2} = 0.6.

Discussion

- Fe-Ti-oxides yield the most accurate a_{TiO_2} estimates without P correction, since they re-equilibrate quickly.
- a_{TiO_2} ~ 0.2-0.3 yields more reasonable Ti-in-zircon T_{xtal} at Mount Pinatubo.
- Matrix glass compositions yield sufficiently low a_{TiO_2} only when magmatic T ~ 780°C and a pressure correction is applied. However, at slightly lower T of ~ 750°C, which is in better agreement with zircon saturation T, the calculated a_{TiO_2} is too high.

Summary

- REE+Y, U+Th and Zr/Hf show positive covariation with Ti concentration in zircon, and are unlikely to be contributing to Ti-in-zircon geothermometry.
- Co-existing Fe-Ti-oxides yield a_{TiO_2} ranging 0.23-0.32. These values are lower than the a_{TiO_2} (≥ 0.6) commonly assumed for crustal magmas.
- Use of a_{TiO_2} = 0.23-0.32 yields T_{xtal} ~ 780°C, which is similar to T based on mineralogy. This suggests that precise estimate of a_{TiO_2} and Ti in the melt is important for obtaining correct T_{xtal}.
- There is a discrepancy between a_{TiO_2} calculated using Fe-Ti-oxides and matrix glass. Overestimated a_{TiO_2} using matrix glass can most likely be explained by lower P in Mount Pinatubo magma reservoirs (~ 2 kbar) relative to the method of Hayden et al. (2007) (calibrated at 10 kbar).
- Based on the common assumption of a_{TiO_2} ≥ 0.6, the Ti-in-zircon geothermometer yields low T by > 100°C for the eruption products at Mount Pinatubo.
- Ti-in-zircon geothermometry applied to ancient zircons using a_{TiO_2} ≥ 0.6 may yield large errors.

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